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ABSOLUTE CROSS-SECTIONS FOR DISSOCIATIVE ELECTRON ATTACHMENT IN O₂ CONDENSED ON KR FILMS

By

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**Absolute cross section for dissociative electron attachment
in O₂ condensed on Kr film**

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Abstract

The absolute dissociative-electron-attachment cross section for O₂ condensed on a Kr film is found to be about 20 times larger than that for gaseous O₂. This large enhancement is attributed to a downward energy shift (≈ 0.9 eV) of the O₂⁻(²H_g) intermediate state due to electronic polarization of the neighboring Kr atoms. Based on the theory developed by O'Malley (Phys. Rev. 150, 14(1966) and 155, 59(1967)], we have shown that this downward shift increases the dissociative attachment by a factor of 21, through a reduction in the autoionization of the intermediate state.

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The simplest system imaginable for studying surface effects might be closed-shell molecules condensed on a rare-gas film. The weak interaction between the closed-shell molecules and the rare-gas surface means most of the spectroscopic data for this system are similar to those of molecules in the gas phase. Hence, one can easily identify the spectroscopic features and recognize changes for the condensed system. The observed changes include parallel shifts of the spectral peaks, changes in the relative intensities, and/or the appearance of new peaks.¹ To our knowledge, however, a comparison between the absolute electron scattering cross sections for a molecule on a solid surface and a molecule in gas phase has not been made. In this letter, we report the absolute dissociative-electron-attachment cross section for O₂ condensed on a Kr film and compare it with that for gaseous O₂. We have found a surprisingly large enhancement of the dissociative attachment cross section when O₂ is placed on a Kr film. We shall explain this large enhancement semi-quantitatively with the theory developed by O'Malley.^{2,3}

Using low-energy electron transmission (LEET) spectroscopy, two of us (M.D. and L.S.) with Marsolais⁴ have devised a new method to measure surface charges on a thin dielectric film deposited on a metal substrate. In a LEET experiment,⁵ the electron current arriving at the metal substrate is measured as a function of the potential applied between the substrate and the electron source. When the dielectric film is not charged, the electron current rises sharply at the zero-energy reference (ZER) of the vacuum level. When electrons are trapped on the dielectric film surface, this ZER shifts to a higher accelerating voltage because the trapped negative charges

retard the incoming electrons. This ZER shift, Δ , is related to the total surface charge Q by

$$\Delta = Q L / \epsilon \pi r^2, \quad (1)$$

where r is an average radius of the surface-charge spreading, and ϵ and L are the dielectric constant and thickness of the film, respectively.⁴

Suppose that a dielectric film is partially covered by molecules with a small surface density σ_0 and that only these molecules can trap electrons. After bombarding the film by electrons for a time t , the total surface charge $Q(t)$ trapped by the molecules is given by

$$Q(t) = I \sigma_0 \mu t \quad (2)$$

for small t , where I is the total electron current, and μ is the electron-trapping cross section. The corresponding ZER shift $\Delta(t)$ is given by

$$\Delta(t) = t L I \sigma_0 \mu / \epsilon \pi r^2, \quad (3)$$

and its time derivative at $t=0$, which is denoted by A_S , is given by

$$A_S = d\Delta(t)/dt|_{t=0} = L I \sigma_0 \mu / \epsilon \pi r^2. \quad (4)$$

Relation (4) was examined in earlier work,⁴ and the proportionality with L , I , and σ_0 was found to be valid. No charge accumulation was

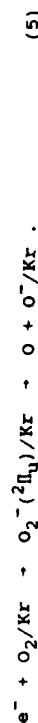
observed on pure Kr films in these experiments for thickness of 1-20 monolayers (ML) in the energy range 4-10 eV.⁴

In the present experiment, Kr gas is leaked in front of a polycrystalline Pt sheet held at 20 K. The number of atoms admitted into the ultra-high vacuum chamber is determined by the gas-volume-expansion dosing procedure.⁵ The film thickness of 20 ML is estimated within 15% accuracy by monitoring the interference structures in LEIS spectra as previously described.⁶ From this calibration, the amount of leaked Kr atoms is known and the O₂ coverage (i.e., 1/7 ML) is determined from this within an accuracy of 15% after verifying that the sticking coefficient of O₂ on Kr and Kr on Kr are the same at 20 K. Since Kr atoms condense in a fcc structure of cell parameter a equal to 5.653 Å having a preferential (111) surface,⁷ we have $L=20 \times 3^{-1/2} a$ and $\sigma_0=(1/7) \times 4 \times 3^{-1/2} a^2$ for the present experiment. The dielectric constant of the Kr film is known⁸ to be $(1.78 \pm 0.01) \times 8.854 \times 10^{-12}$ Farad/m.

The absolute value of the incident current ($I=5 \times 10^{-9}$ A) is measured by allowing all electrons, including those reflected, to return to the surface according to the method described previously.⁵ The beam profile is recorded by intercepting a small percentage of the incident electrons with a thin wire scanned in the plane perpendicular to the electron velocity. The average radius of the beam is found to be $(3.7 \pm 0.3) \times 10^{-4}$ m. Bombarding the O₂/Kr film with 6.0-eV electrons having these electron-beam characters, we find $A_S=(1.1 \pm 0.1) \times 10^{-2}$ Volt/sec. We expect the average radius of the surface charge to be approximately equal to the beam radius i.e.,

$r=3.7 \times 10^{-4}$ m. Substituting these (I , r , and A_S) data and those (L , σ_0 , and ϵ) given in the previous paragraph into Eq. (4), we obtain $\mu=2.2 \times 10^{-17}$ cm² for 6.0-eV electrons. Since the electron-energy dependence of μ exhibits a broad peak around 6 eV,⁴ this μ value corresponds to the maximum.

It has been shown⁹ that, for electron energies 4-7 eV, the charges produced on the surface of O₂/Kr are O⁻ ions arising from dissociative attachment (DA) via the O₂⁻(² Π_u) intermediate state:



It is also known¹⁰ that some of the O⁻ ions produced via the same process can escape from the Kr surface. If we know the fraction (f) of the desorbing O⁻, we can obtain the DA cross section (σ_{DA}) from the μ , since they are related by $\mu=(1-f)\sigma_{DA}$. In the gas phase, the DA proceeds via the same intermediate state, O₂⁻(² Π_u).¹¹ The cross section for this process reaches a maximum of $(1.3 \pm 0.2) \times 10^{-18}$ cm² at 6.7 eV.¹² Comparing this maximum with the corresponding maximum for O₂/Kr given above, we conclude that the maximum DA for O₂/Kr is about $17/(1-f)$ times larger than that for gaseous O₂, where $0 < f < 1$. In the remaining sections of the paper, we shall present an explanation for the origin of this large enhancement.

Figure 1 shows schematically how a Kr film influences the DA process. The upper curves illustrate the accepted interpretation of the DA process for gaseous O₂: The intermediate state O₂⁻($1\pi_g^{-1}\pi_g^{-4}$)² Π_u dissociates into the lowest O+O⁻ limit, competing with

autoionization into the $1^3\Sigma_u^+$, c^3A_u , and $c^1\Sigma_u^-$ states arising from the excited configuration $O_2^*(1\pi_u^3 1\pi_g^3)$ and into the $b^1\Sigma_g^+$, a^1A_g , and $x^3\Sigma_g^-$ states arising from the ground configuration $O_2(1\pi_u^4 1\pi_g^2)$. The three states arising from the excited configuration are close to each other and hence are represented in the figure by a single potential curve. (The $1^3\Sigma_u^+$, $3^3\Sigma_u^-$, and 1^1A_u states arising from the $O_2^*(1\pi_u^3 1\pi_g^3)$ configuration have higher energy than the autoionizing $O_2^-(^2\Pi_u)$ state.) According to O'Malley,³ only a tiny fraction ($\approx 1.3\%$) of the $O_2^-(^2\Pi_u)$ states dissociates into the $O+O^-$ limit. The majority of the $O_2^-(^2\Pi_u)$ states autoionize into the three states arising from the excited configuration, and the remainder into the three states arising from the ground configuration. (Autoionization into the three states arising from the excited configuration is much faster than that into the states arising from the ground configuration, since the former is a one-electron process while the latter is a two-electron process.)

The theoretical expression for the DA cross section is known, for example, to be Eq. (5.24) of Ref. 2. Further, the potential curve for the $O_2^-(^2\Pi_u)$ intermediate state and its survival probability against autoionization have been determined by O'Malley³ and confirmed by Henderson et al.¹³ From this information, we can calculate the necessary quantities for evaluating the DA cross section. We obtain

$$\sigma_{DA} \propto \exp[3.4(R_C - R_E)^2 - 376(R_E - R_E)^2 - 41(R_C - R_E)^{3/2}], \quad (6)$$

where R_E is the turning point (in Å) of the $O_2^-(^2\Pi_u)$ intermediate

state at the incident-electron energy E ; R_C (≈ 1.44 Å), the crossing point between the potential curves of the $O_2^-(^2\Pi_u)$ state and the $O^*(1\pi_u^3 1\pi_g^3)$ states; and R_E , the equilibrium internuclear distance (1.21 Å) of the O_2 ground state. The first two factors in Eq. (6) arise from the Franck-Condon overlap integral between the vibrational ground state of the O_2 ground state and the vibrational continuum of the repulsive $O_2^-(^2\Pi_u)$ state. The delta-function approximation¹⁴ yields the second factor, and the first factor is the first-order correction.² The third factor represents a survival probability of the $O_2^-(^2\Pi_u)$ intermediate state against autoionization.³ The proportionality constant is nearly independent of the electron energy E ,^{2,3} so that it is also nearly independent of R_E . The σ_{DA} reaches a maximum at $R_E = 1.244$ Å, which corresponds to $E = 6.9$ eV.

When an O_2 molecule is placed on the Kr film, as shown in the lower half of the figure, the potential curves for the neutral states remain virtually the same, but the potential curve of the charged state $O_2^-(^2\Pi_u)$ is shifted downward in parallel, because of an electronic polarization of the neighboring Kr atoms. Note that the dissociation limit $O+O^-$ is split into the $O/Kr+O^-$ and $O+O^-/Kr$ (or $O/Kr+O^-/Kr$) limits, and that the former limit has approximately the same energy as the $O+O^-$ limit and the latter limit is lower than the former limit by an amount equal to the polarization energy. The downward shift of the $O_2^-(^2\Pi_u)$ intermediate state does not affect the R_E value and the coefficient 376 of Eq. (6) but does affect directly the values of R_E and R_C . The coefficients 41 and 3.4 and the proportional constant are expected to be virtually unaffected upon a

parallel-energy shift of the intermediate state. Thus, to evaluate σ_{DA} for O_2/Kr , all we need is the polarization energy and the corresponding R_C value.

The surface-polarization energy of the Kr film appears to be about 0.9 eV. A comparison between the observed threshold energies (4.4 eV¹¹ and 3.5 eV⁶) of the O^- yield from gaseous O_2 and the O^-/Kr trapping for O_2/Kr gives 0.9 eV for the surface polarization of the Kr film. A theoretical estimate of this energy gives 0.86 eV, half of the calculated bulk polarization energy,¹⁵ supporting the observed shift. To calculate R_C for O_2/Kr , we use the empirical $O_2^-(^2\Pi_u)$ potential curve³ but shifted downward by 0.9 eV. The $O_2^*(1\pi_u^3 1\pi_g^3)$ potential curve is determined by assuming that it is quadratic having a minimum at $R=1.52$ Å as observed;¹⁶ has the experimental vertical excitation energy of 6.1 eV;¹⁷ and intersects the $O_2^-(^2\Pi_u)$ curve at $R=1.44$ Å as found³ empirically. The resultant R_C for O_2/Kr is 1.295 Å. With this new R_C , Eq. (6) has a maximum at $R_E=1.230$ Å, which corresponds to $E=6.4$ eV assuming the 0.9-eV shift.

With this preparation, we can now calculate the ratio of the DA cross sections for O_2/Kr and gaseous O_2 at their maxima:

$$\sigma_{DA}(O_2/Kr) / \sigma_{DA}(\text{Gaseous } O_2) = 21. \quad (7)$$

This ratio is sufficiently large to account for the observed ratio, 17/(1-f), and also suggests that $f=0.19$ (i.e., 19% of the O^- desorbs), which is reasonable. Therefore we attribute the observed

enhancement to the downward shift (≈ 0.9 eV) of the O_2^- intermediate state relative to the O_2 states. This calculation also indicates that the enhancement is due to a reduction in the autoionization rate when O_2 is placed on the Kr film.

Finally, we exclude two possible explanations for the observed enhancement: (i) Unlike gaseous O_2 , the orientation of the O_2 on the Kr film is fixed. The O_2 orientation dependence can be calculated from the angular distribution of O^- from gaseous O_2 , which has been measured by Van Brunt and Kieffer.¹⁸ This calculation shows that the maximum enhancement is 1.3 when every O_2 on Kr surface is tilted 40° from the surface. (ii) An incident electron could enter a surface state of the Kr film, enhancing the electron capture to the O_2^- state. However, in our experiment, we cannot excite any surface states, because the incident electron energy (6 eV) is too low for our normal-incident electrons to enter even the lowest surface state of the Kr film.

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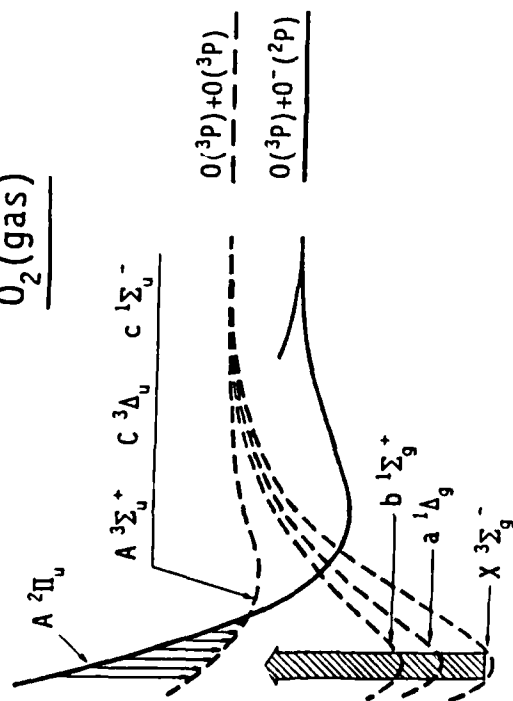
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Figure caption

Fig. 1. Schematic potential-energy curves of O_2^- (solid curves) and O_2 (dashed curves) states for gaseous O_2 (top) and O_2 physisorbed on a Kr film (bottom). When O_2 is placed on a Kr film, the potential curve of the $O_2^-(A^2\Pi_u)$ state is shifted downward with respect to potential curves of the O_2 states. Autoionization of the $O_2^-(A^2\Pi_u)$ and $O_2^-(A^2\Pi_u)/Kr$ states are indicated by downward arrows.

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 $O_2(\text{gas})$  O_2/Kr 